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Bringing Science Solutions to the World

Modeling of Materials and Synthesis of Model Materials

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Overview

Timeline

- October 1st 2019 - September 30st 2022.
- Percent complete: 30%

Budget

- Funding for FY 19: $540K
- Funding for FY 20: $500K
- Anticipated total funding: $1,620K

Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals
  - Cost, Performance and Safety

Partners

- Bryan McCloskey (LBNL)
- Robert Kostecki (LBNL)
- Guoying Chen (LBNL)
- Gerbrand Ceder (LBNL)

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Relevance

Impact:

Modeling research will aim to understand and suggest improvements for

- Li-ion conduction in non-aqueous, super-concentrated electrolytes

- Li-ion conduction and oxygen transport in amorphous oxide coating materials

- SEI formation on Li metal anodes in Gen II - based electrolytes

Objectives:

- Identify Li-ion and oxygen conduction mechanisms in amorphous oxide coatings to suggest improved formulations

- Identify solvation environments, viscocity and conduction mechanisms in super-concentrated nonaqueous electrolytes, and propose changes to solvent/salt compositions to improve active ion conductivity

- Identify reaction pathways in SEI formation on Li metal anodes in Gen II liquid electrolytes from high-throughput first-principles simulations of the reaction cascade with associated machine-learning approaches.

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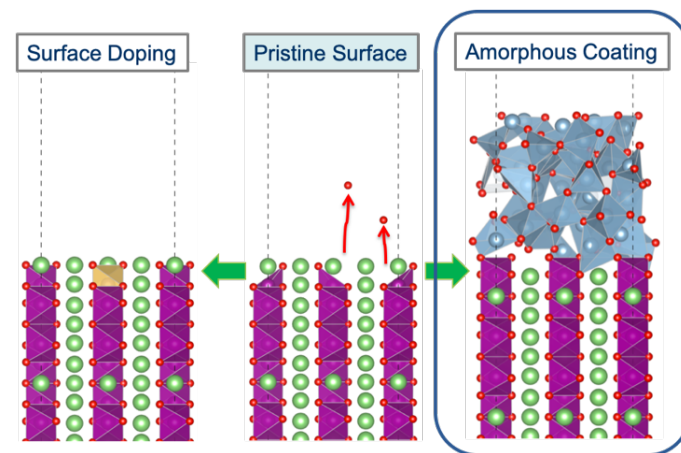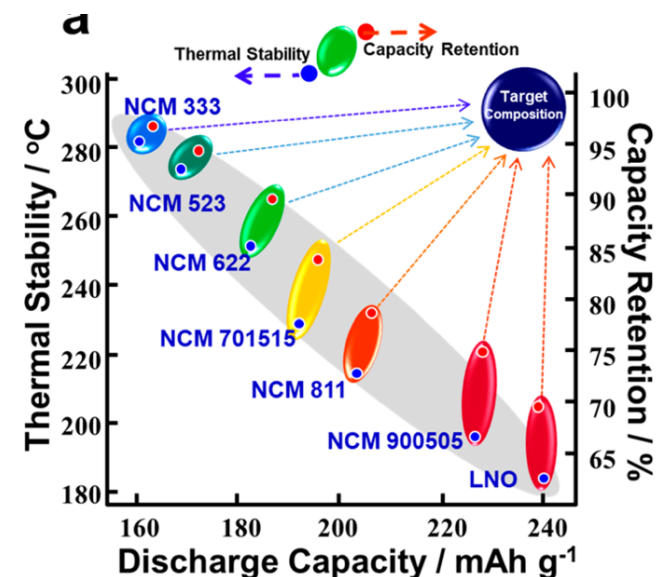
Approaches and Techniques

$$F=ma$$

$$i\hbar \frac{d\Psi(\{r_i\};t)}{dt} = \hat{H}\,\Psi(\{r_i\};t)$$
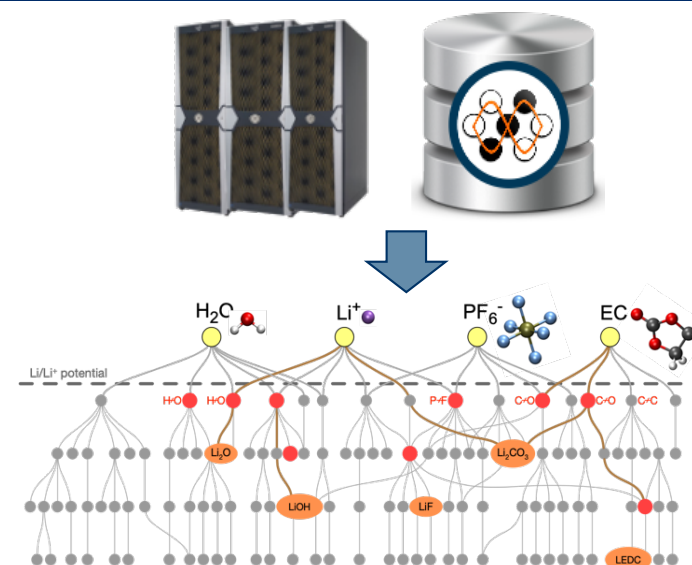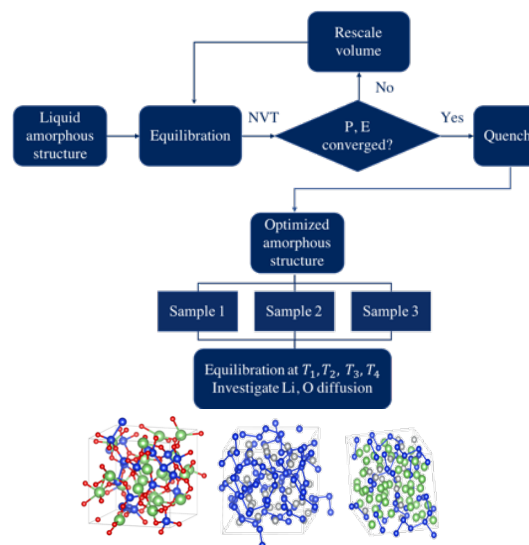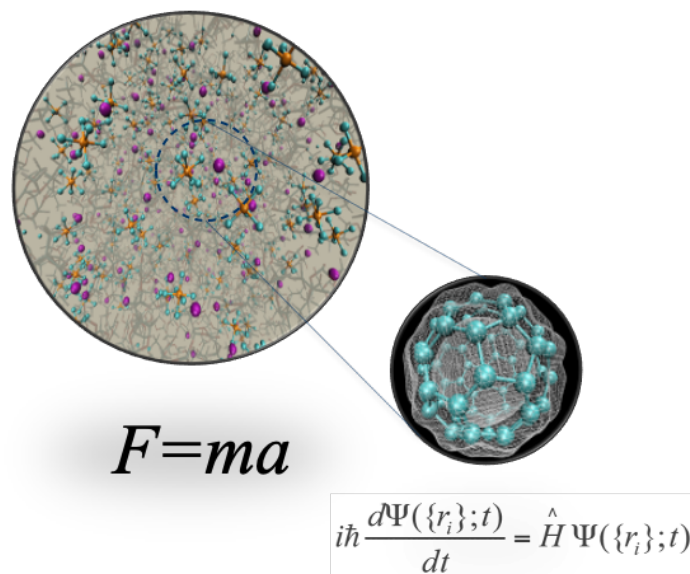
- Larger non-reactive systems which need long equilibration time (e.g. solvation structures) are treated with semi-empirical classical molecular dynamics

- Electrochemical and chemical reactions are treated with first-principles, quantum mechanical methods (VASP, Gaussian). Crystal orbital Hamiltonian populations (COHP) are used to extract chemical interactions between atoms from band structure calculations.

- Amorphous solids are obtained through ab-initio molecular dynamics and a melt-quench process (see flow diagram: right)

- High-throughput first-principles calculations of molecular reactions, with associated machine-learning to accelerate fragmentation/recombination information.
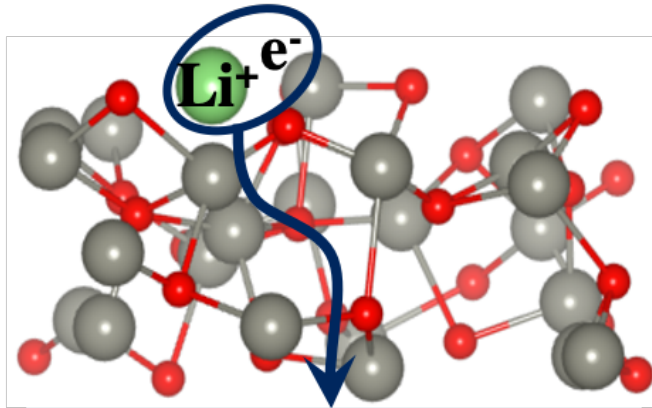
Milestones

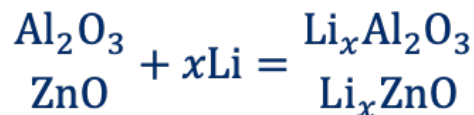| Month/Year	Milestones	Status
December 2019	Obtain desirable chemical and structural traits of amorphous cathode coatings	Completed
March 2020	Identify the Li diffusion bottlenecks in two known coating materials	Completed
June 2020	Quantify the conduction mechanisms in superconcentrated $LiPF_6/PC$	Completed
September 2020	Preliminary insights into the SEI composition and reaction pathways for baseline electrolytes. First approximative reaction scheme proposed.	Ongoing

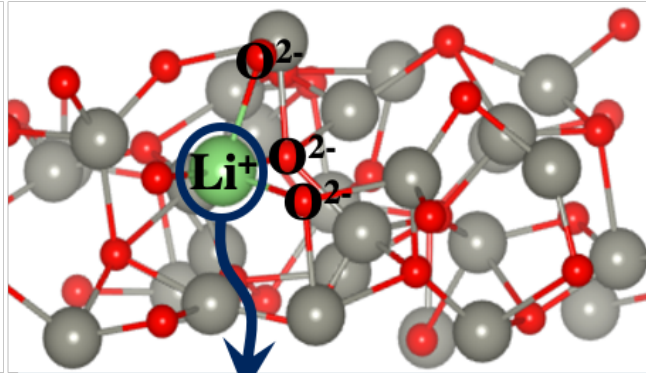# Technical Accomplishments and Progress: Li Transport Models in Thin Coatings
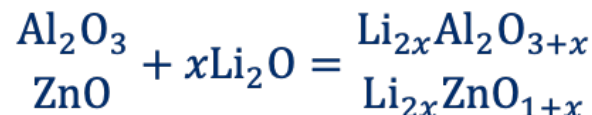

(a) Electron conducting model

$$\begin{matrix} Al_2O_3 \\ ZnO \end{matrix} + xLi = \begin{matrix} Li_xAl_2O_3 \\ Li_xZnO \end{matrix}$$

(b) Electrolyte model

$$\begin{matrix} Al_2O_3 \\ ZnO \end{matrix} + xLi_2O = \begin{matrix} Li_{2x}Al_2O_{3+x} \\ Li_{2x}ZnO_{1+x} \end{matrix}$$

(c) Space charge model

$$\begin{matrix} Al_2O_3 \\ ZnO \end{matrix} + xLi^+ = \begin{matrix} Li_x^+Al_2O_3 \\ Li_x^+ZnO \end{matrix}$$
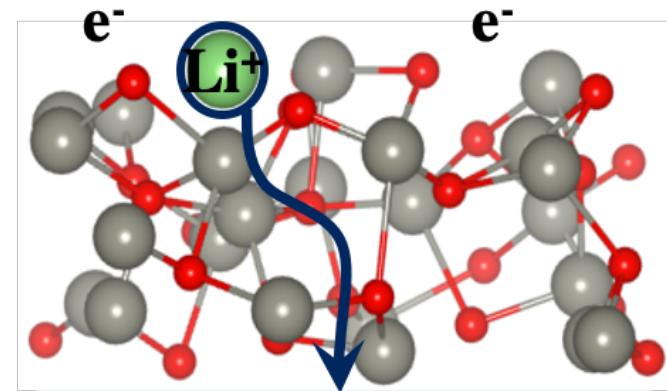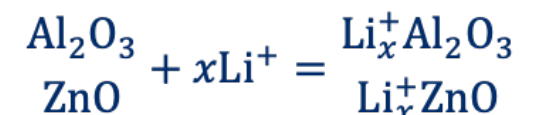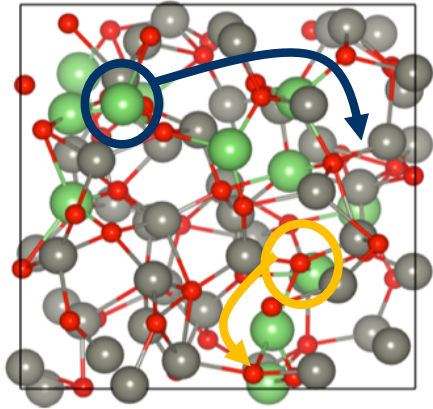
electric field (Li+ space charge) >> breakdown field of coating

a) **Electronically conducting coating** does not contain Li, **electron accompanies Li$^+$ diffusion and coating cation is reduced** during Li diffusion.

b) **Electronically insulating coating** incorporates **Li$^+$** with compensating negative charge − (e.g. LiAlO$_2$): **coating cation is not reduced** during Li diffusion.

c) **Li$^+$** tunnels through **electronically insulating coating,** without electron − with space charge build-up.

J. Phys. Chem. Lett., 4:2681, 2013; Chem. Mater. 2004, 16, 639-645
Adv. Mater., 23:3911–3915, 2011; Xu et al. J. Mater. Chem. A, 2015, **3**,17248

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To analyze how Li and O move through an amorphous solid we built an analyses framework to extract the chemical coordination environments where the ions get 'stuck'? Analyzing the trajectory and how the ions move showcases what coordination environments cause diffusion bottlenecks.

Yellow dots: vibrational motions
Green dots: translational motions

Li trajectory through amorphous solid
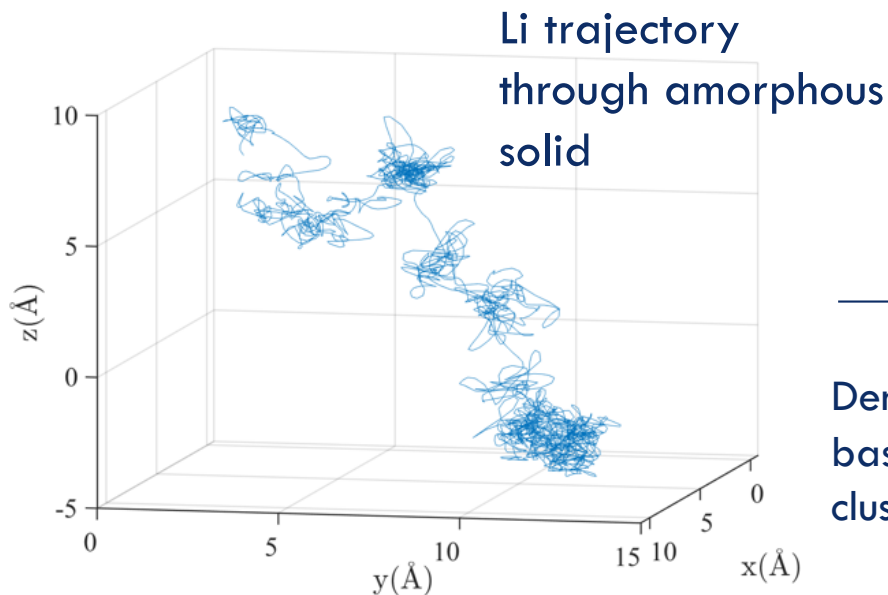
Density-based spatial clustering

Identification of vibration and translational motion
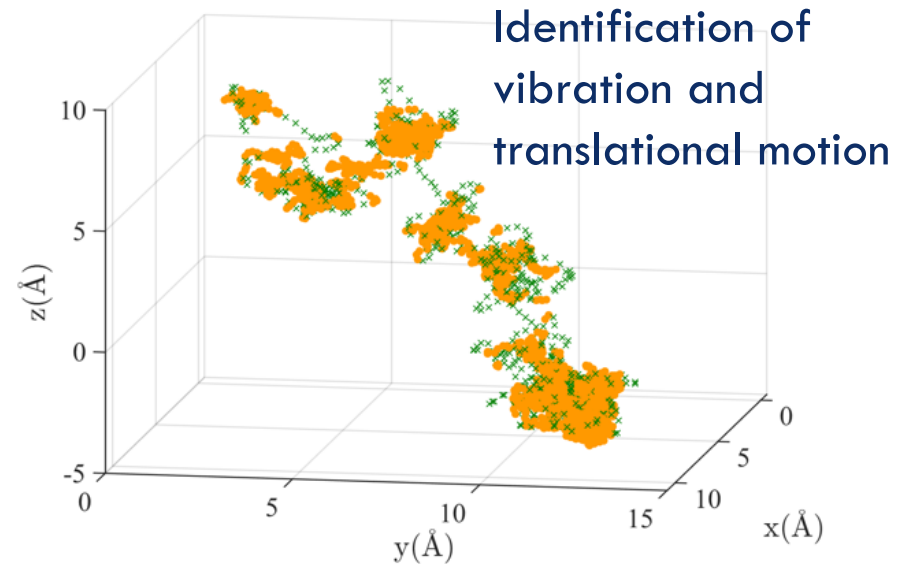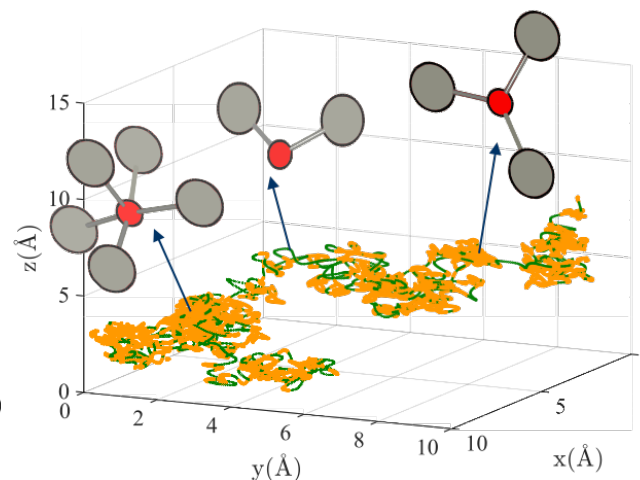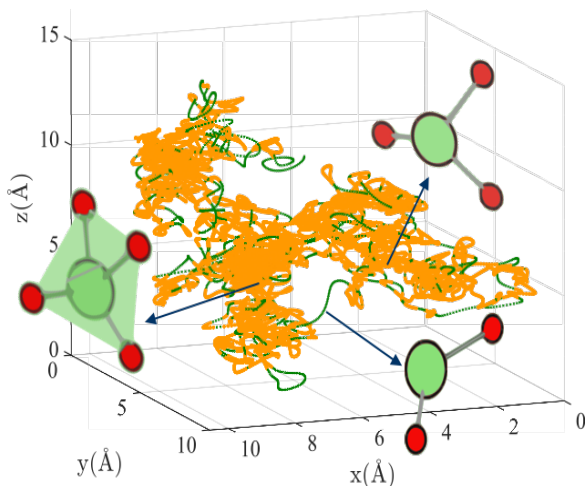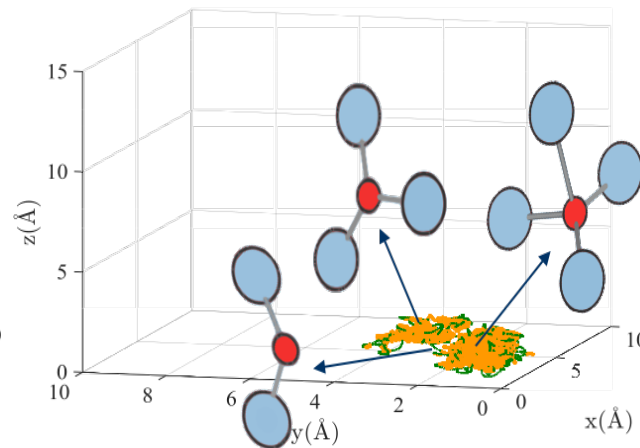
Large fractions of vibrational motions as compared to the translations motions signifies low conductivity and allows us to find the coordination environments where the ionic species get stuck.

- Li^+ diffusion is limited by strongly bonded O^{2-} coordination
- O^{2-} diffusion is limited by the $Al^{3+}(Zn^{2+})$ coordination environments
- Microscopic mechanism of ionic conduction:

  Ionic hopping between the trapping sites is accompanied by *bond breaking/forming processes.*

(a) — D_{rt}^{Li} (cm^2/s) vs Li concentration (%); ZnO, Al$_2$O$_3$
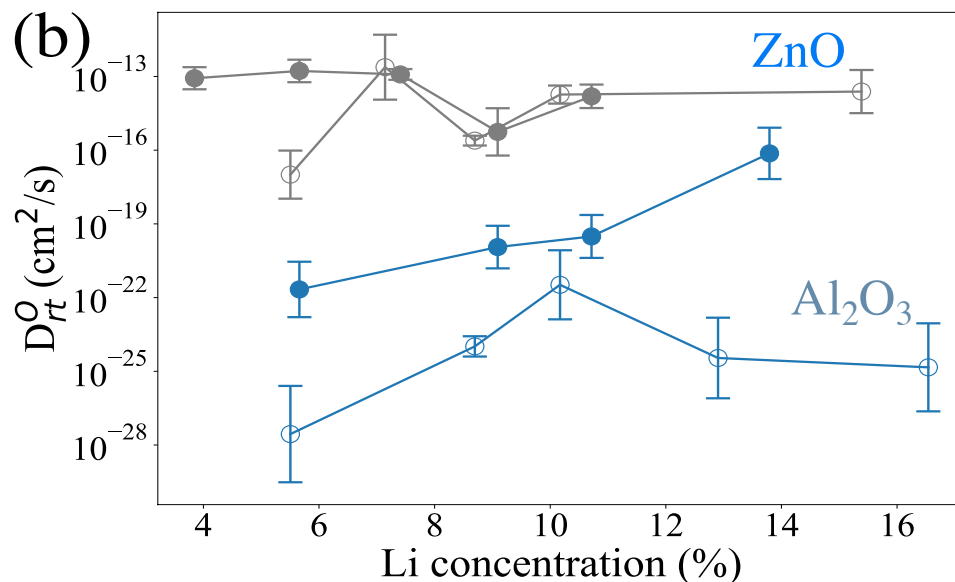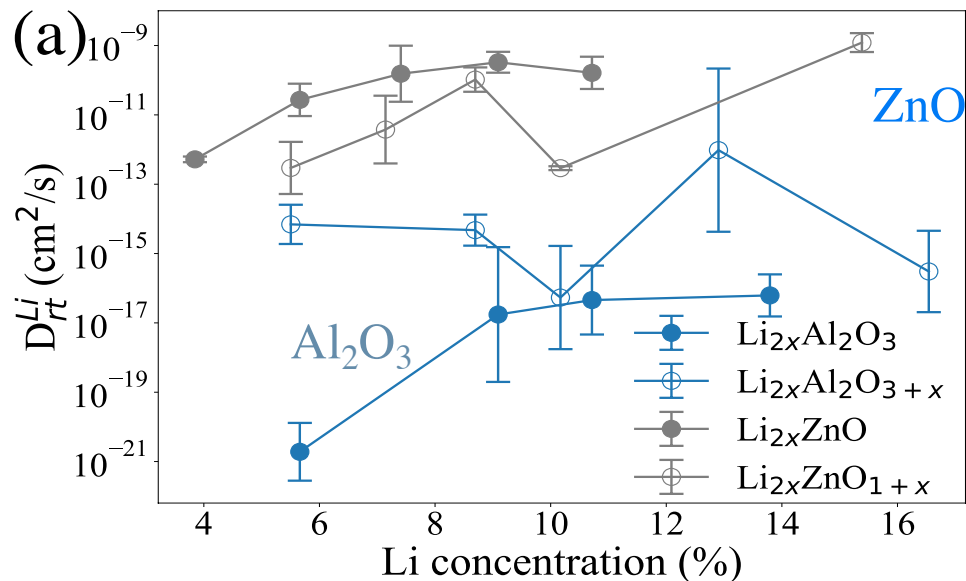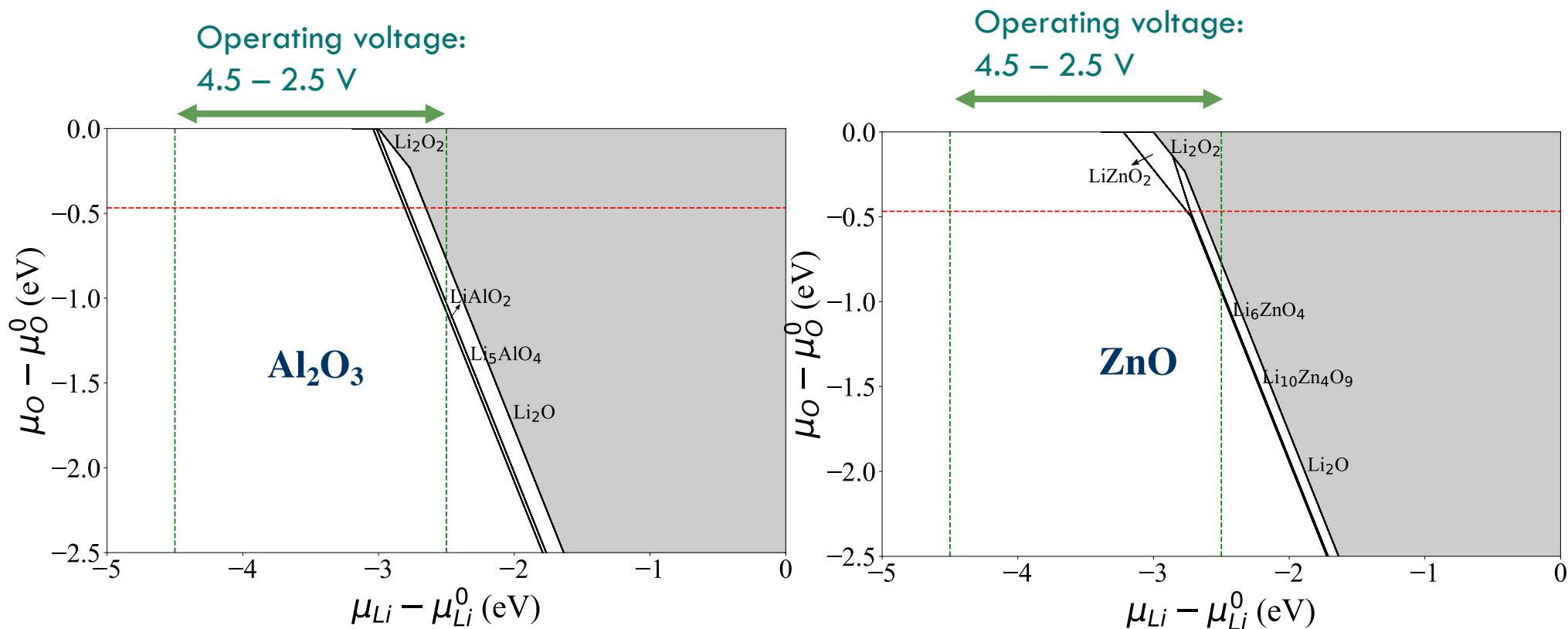
Legend:
- Li$_{2x}$Al$_2$O$_3$
- Li$_{2x}$Al$_2$O$_{3+x}$
- Li$_{2x}$ZnO
- Li$_{2x}$ZnO$_{1+x}$

(b) — D_{rt}^{O} (cm^2/s) vs Li concentration (%); ZnO, Al$_2$O$_3$

- In general, a higher Li$^+$ concentration trends with increasing Li and O diffusivity.
- The 'electrolyte' model promotes faster Li$^+$-ion diffusion in Al$_2$O$_3$; whereas in ZnO no major difference between conduction mechanisms is observed. This result suggests that electron mobility is not a bottleneck for Li+ conductivity in ZnO, whereas in Al$_2$O$_3$ it is.
- **Both Li$^+$ and O^{2-} diffuse much faster in ZnO than in Al$_2$O$_3$**
- Li-ion conductors, such as LiAlO$_2$ and Li$_6$ZnO$_4$, is hence predicted as better coating candidates from a Li-conductivity perspective.

J. Phys. Chem. C 2007, 111, 4061-4067; Chem. Mater. 2014, 26, 3128−3134; Solid State Ionics 40/41 (1990) 13-17

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While we predicted that lithium-containing coatings such as $LiAlO_2$ and Li_6ZnO_4 exhibit higher Li+ conductivity, here we find that these materials would not be stable against a cathode at high charge state. In fact, they will be delithiated to Al_2O_3 or ZnO. Hence only Li+ containing materials that show exceptional stability against Li extraction (per the phase diagram analysis shown) should be considered for the next-generation coatings.

Integrated COHP: $ICOHP = \int^{E_F} pCOHP(E)\, dE$
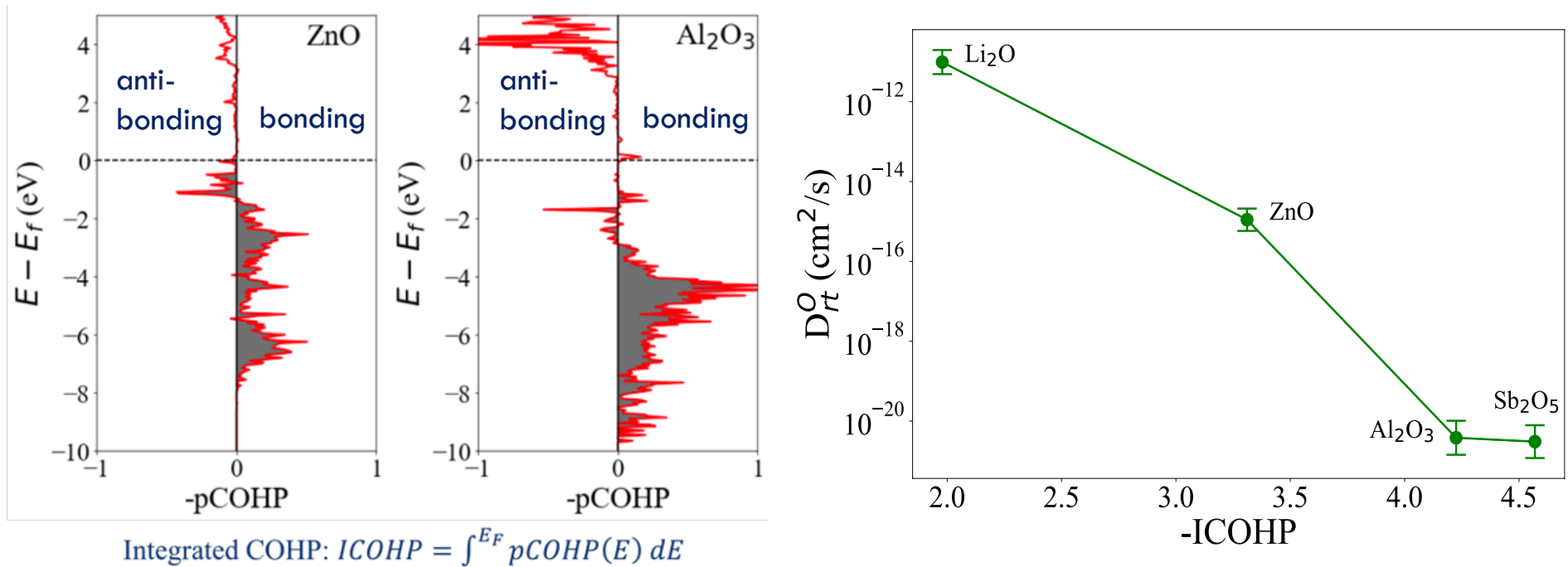
We previously established that both Li^+ and O^{2-} diffuses through bond breaking/formation processes in these coating materials. Hence, we hypothesize that stronger bonds should correlate with lower diffusivity. Using local bond analyses, we find that – indeed - the low O^{2-} diffusivity in Al_2O_3 is due to the stronger bonding environments as compared to ZnO. This metric will help us locate better oxygen-retention coatings.

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$$L_c = 1nm$$

Li$^+$
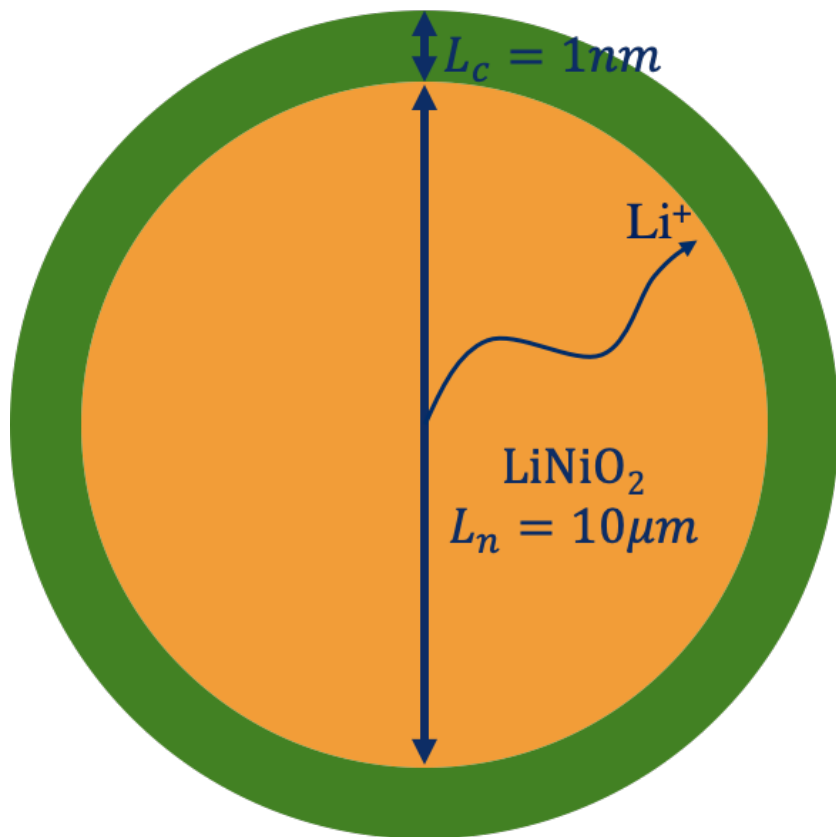
LiNiO$_2$
$$L_n = 10\mu m$$

$$t = \frac{l^2}{D}$$

D (cm²/s)	L (nm)	t (s)
$D^{Li}_{LiNiO_2} = 10^{-10}$	10^4	2500
$D^{Li}_{Al_2O_3} = 10^{-16}$	1 to 10	100 to 10^4
$D^{O}_{Al_2O_3} = 10^{-20}$	1	10^6
$D^{Li}_{ZnO} = 10^{-10}$	1	10^{-4}
$D^{O}_{ZnO} = 10^{-14}$	1	1

We compare the diffusion times of Li$^+$ and O^{2-} through a coating with a specified thickness to that of Li through a LiNiO$_2$ 10 micrometer particle. Using a simple 1D diffusion model, we find that Al$_2$O$_3$ only exhibits good Li$^+$ diffusion properties while impeding O^{2-} transport if the coating is uniform with a very thin thickness =< 1 nm. ZnO exhibits better Li$^+$ diffusion but fails to impede O^{2-} transport, even for thicker coatings.

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Quantum Mechanical HT
infrastructure and Supercomputers

> 10,000 molecules

> 140,000 elementary reactions

High-throughout computational infrastructure has resulted in world-leading available molecular and reaction network, covering over 140,000 elementary reactions. Graphical representation is utilized to analyze the reaction pathways.
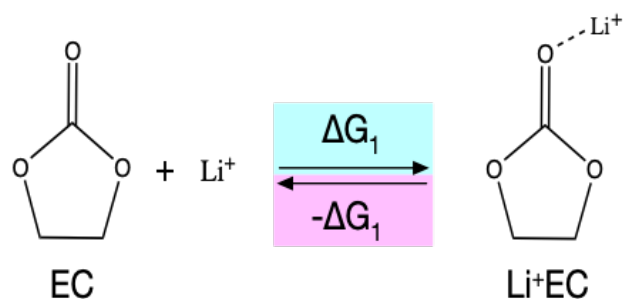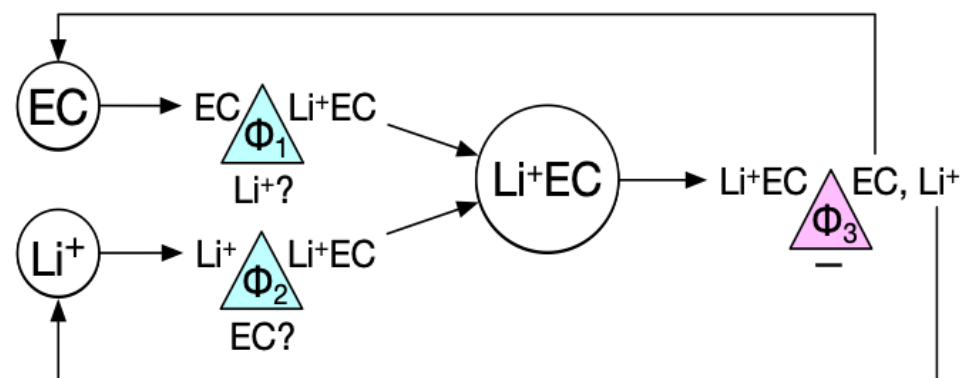
Graph representation

Transformation of conventional reactions into graphical representations, where species and combinations of species are nodes, and reaction Gibbs free energies are transferred into cost functions allow us to analyze favorable thermodynamic pathways.

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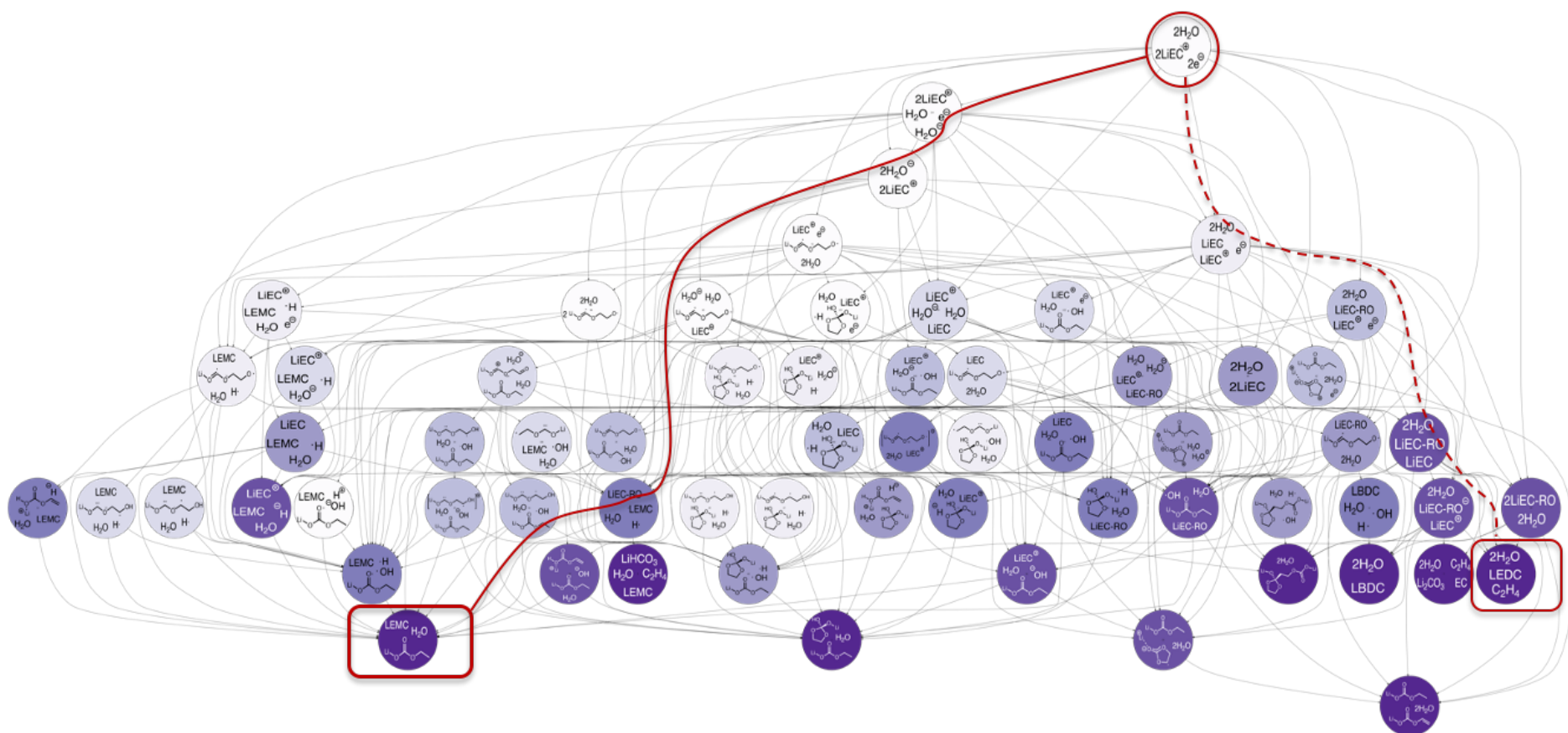
Using the large database of calculated bond formation and bond breaking energetics, we can predict downhill reaction pathways and analyze differences between them. Here we show a preliminary and limited version where we can observe the differences in forming LEDC vs LEMC from the initial reduction of Li+-coordinated EC and following reactions.

MAGNN feature update mechanism

update atom features

update global state features

update bond features

u — global state features
b_j — features of bond j
a_i — features of atom i
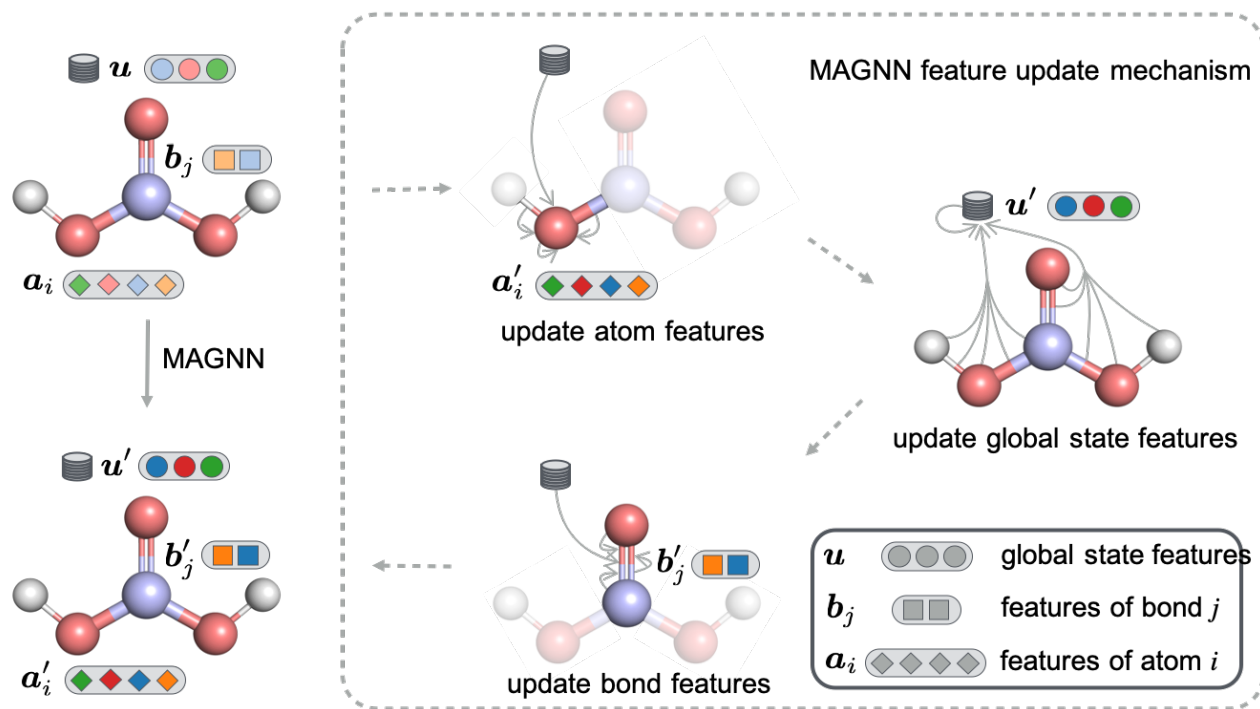
Even with supercomputers, it is too expensive to explicitly calculate all possible bond breaking and bond formation reactions in this large network. Hence, we have trained a machine learning model to predict molecular bond formation energies, using local bond topology and speciation as well as global charge of the molecular fragment. The results are very encouraging with over 90% recall, precision and f1 scores.

|	stable	unstable
recall	0.93	0.96
precision	0.95	0.94
f1 score	0.94	0.95

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Responses to Previous Year Reviewers' Comments

Presentation ID	Presentation Title	Principal Investigator (Organization)	Page Number	Approach	Technical Accomplishments	Collaborations	Future Research	Weighted Average
bat091	Predicting and Understanding Novel Electrode Materials from First Principles	Kristin Persson (LBNL)	2-28	3.63	3.63	3.88	3.50	3.64

Examples: *"The reviewer also found that results obtained on Li mobility in highly concentrated liquid electrolytes using first principles, semi-empirical molecular dynamics, and static computational approaches is very relevant and useful for designing novel Li-ion rechargeable batteries with low cost, high capacity, energy density, and safety. "*

"The reviewer indicated there were very strong technical accomplishments and encouraged the PI to focus some future work on the Si-SEI, which remains at the heart of the cycle, and calendar-life issues with Si-containing cells. "

"The reviewer stated it was highly relevant with very good focus. "
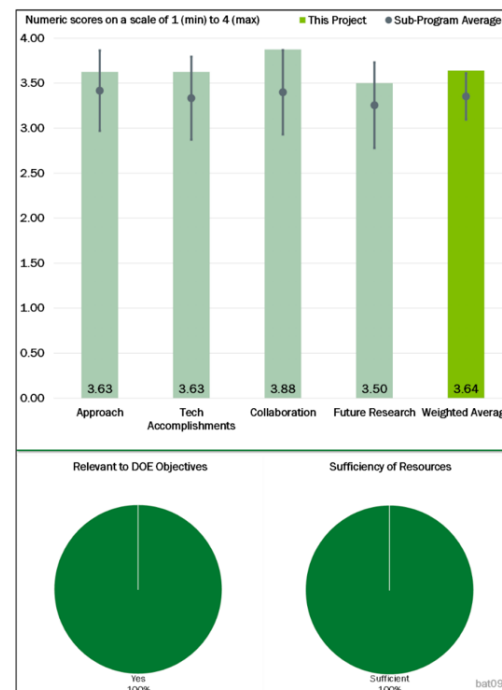
Partners and Collaborations

We are excited that some of our coating formulations is considered by our partners at LBNL; Guoying Chen and Gerbrand Ceder, for high-voltage cathodes.

The insights from the SEI reaction cascade on the Li metal anode will be compared to model materials and spectroscopic results by Robert Kostecki.

Collaborations on electrolyte formulations are ongoing with Bryan McCloskey, LBNL and Brett Lucht, U Rhode Island.

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Summary and Future Work

- We find that Li and O diffusion in model systems Al_2O_3 and ZnO are related to the coordination number and strength of bonded O ion and Al (Zn), respectively. Li and O diffuse both much faster in ZnO than in Al_2O_3. Considering both Li^+ diffusivity as well as oxygen transport as selection metrics, Al_2O_3 provides a better conformal, thin, cathode coating than ZnO, however, the coating must be very thin to enable reasonable Li conductivity. Although the lithiated versions of Al_2O_3 and ZnO, such as $LiAlO_2$, can achieve a faster Li^+ diffusion, they are not stable against delithiation at a state of high charge. We will use these insights to simulate other Li-containing systems, in particular systems which retain Li at high charge and bind oxygen more strongly, to identify novel coating formulations with high Li conductivity and low O conductivity.

- We have built the high-throughput infrastructure to calculate thousands of molecular fragments to enable the calculation of a reaction cascade of over 100,000 possible reactions. We are formulating the reaction cascade as a graphical network and are using machine learning to predict bonds breaking/formations that are not yet in the database. We are on track to produce the first results of early SEI formation reaction pathways in a model system such as $LiPF_6$ in EC on Li metal by September 2020.

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Publications/Presentation

Publications

- Jianli Cheng, Eric Sivonxay, Kristin A. Persson, *Evaluation of Amorphous Oxide Coatings for High-voltage Li-ion Battery Applications using a First-Principles Framework*, under review in ACS Applied Materials & Interfaces, 2020

- Eric Sivonxay, Muratahan Aykol, Kristin A. Persson, *The lithiation process and Li diffusion in amorphous SiO2 and Si from first-principles,* Electrochimica Acta Volume 331, 2020, 135344, 10.1016/j.electacta.2019.135344

- Julian Self, Kara D. Fong, and Kristin A. Persson, Transport in Superconcentrated LiPF6 and LiBF4/Propylene Carbonate Electrolytes, ACS Energy Lett. 2019, 4, 2843−2849, 10.1021/acsenergylett.9b02118

Presentations

Gordon Research Conference Ventura, Feb. 17th 2020: "Degradation Mechanisms of High-Nickel Layered Cathodes and Mitigation Strategies Suggested from First-Principles Calculations"; Kristin A. Persson